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Abstract

Full Text

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EFFECT OF SUBSTITUENTS IN THE REACTION OF ELECTROPHILIC BIMOLECULAR SUBSTITUTION

Previously, in studying a series of reactions of ethyl esters of α-bromomercuriarylacetic acids, representing processes of the S_E2 type, it was shown that the effect of substituents does not correspond to the classical concepts of the mechanism of bimolecular electrophilic substitution ([1–3]). This made it possible to suggest that, owing to the lability of the C–Hg bond of this system, an intermediate mechanism between S_E1 and S_E2 takes place; and, although the reaction-rate constant is described by the equation for bimolecular reactions, the effect of substituents corresponds to the S_E1 mechanism ([1,2]).

In the present work the effect of substituents on the rate of reaction of substituted benzylmercury halides with iodine in the presence of cadmium iodide has been studied; this reaction is also an example of electrophilic bimolecular substitution

$$\mathrm{X{-}\langle benzene\rangle{-}CH_2{-}HgY + J_2(CdJ_2) \longrightarrow X{-}\langle benzene\rangle{-}CH_2J + HgYJ(CdJ_2)}$$

As substituents X there were used n-CH_3O, n-CH_3, m-CH_3, o-CH_3, n-F, m-F, o-F, n-Cl, o-Cl, m-Br, n-NO_2; in some cases the anion bound to the mercury atom was varied.

In methanol the reaction was carried out at equimolecular reagent concentrations of $1 \cdot 10^{-3}$ mol/l at 19°C. The reaction follows the second order (Fig. 1). The values of the second-order reaction-rate constants are given in Table 1.

The general order of substituent effects corresponds to a reaction proceeding by the S_E2 mechanism: $CH_3O > CH_3 > H > Cl$. However, it is striking that the reaction-rate constants for para-halo substituents are very close to the constant for the unsubstituted compound, and for n-F the value of K_2 is even somewhat larger; in the case of para-nitrobenzylmercury bromide the reaction in general proceeds instantaneously. Thus, the complete series of effects of para substituents, $CH_3O > CH_3 > H \sim Cl < F \ll NO_2$, is not the usual one and does not agree with the concepts of the S_E2 mechanism. For the electron-donor substituent methyl, the accelerating effect decreases in the series para > ortho

> meta, while for halogens the reaction rate is retarded in the series para > meta > ortho.

Table 1

X	H	CH_3O	CH_3	F	Cl	Br	NO_2
para	–	8.33	1.93	0.84	0.71	–	instantaneously
meta	0.75	–	0.83	0.42	–	0.46	–
ortho	–	–	1.75	0.22	0.23	–	–

First of all, it was necessary to check whether this effect is general for the given reaction under the conditions of other solvents; therefore the reaction of substituted benzylmercury chlorides with iodine in the presence of CdJ_2 was carried out in the aprotic solvent DMF. The kinetic data in DMF also fit the regularities for second-order reactions (Fig. 1b). The order of substituent effects is the same as in methanol: $NO_2 \gg n\text{-}CH_3O > CH_3 > H >$ Hal; within the halogen series, para > meta > ortho; for methyl, para > ortho > meta.

The temperature dependence of the reaction rate in DMF was studied for each compound. The obtained values of the constants, the corresponding temperatures, and also the parameters of the Arrhenius equation found from the plot $\lg K = f\left(\frac{1}{T}\right)$ (Fig. 2) and the calculated activation entropies are given in Table 2.

Table 2

X	T-ra, °K	K_2, l/M· sec	E, kcal/mole	lg A	$-\Delta S$, entropy units	X	T-ra, °K	K_2, l/M· sec	E, kcal/mole	lg A	$-\Delta S$, entropy units
H	2882930323	80.253	12.47	9.7	16.2	m-CH_3	2933033123	30.483	13.88	9.6	16.7
p-CH_3O	2832882913	31.964	12.78	10.6	12.1	m-F	2933033113	20.243	13.48	9.3	17.6
p-CH_3	2933033151	10.954	12.01	10.0	14.8	m-Br	29330330921	1.253	13.920.49	9.3	17.6
p-F	2882930323	30.193	11.80	9.6	16.7	o-CH_3	2933033145	50.834	11.65	9.9	15.3
p-Cl	2882930321	10.164	11.67	9.5	17.1	o-F	29330330881	1.3914	14.250.49	9.2	18.0
p-Br	28829309840	8.1913	13.260.69	9.6	16.7	o-Cl	2933088103	80.254	14.42	9.2	18.0

From the data of Table 2 it is evident that the activation energies for all substituted compounds are identical within the limits of experimental error, i.e., the

difference in rates is determined only by changes in the pre-exponential factor. These changes are very small (the largest deviation is 1.4) and often occur only in the second decimal place (as, for example, in the case of p-Br and m-CH_3), which we neglect; however, the reaction rates are quite distinguishable, and the general course of the dependence $\lg K = f\left(\frac{1}{T}\right)$ indicates the validity of the conclusion drawn.

Fig. 1. Plot of the dependence $d_0/d - 1 = f(\tau)$ for X = $C_6H_4CH_2HgCl$ in methanol at 20° (A); and in DMF at 20° (B)

This result is not entirely usual, since the change in polarity of the compound upon introduction of a substituent into the benzene ring should be expressed primarily in a change in the activation energy. Because for para-substituents spatial influence is of no importance, while the changes in rate are nevertheless connected only with a change in entropy, it may be assumed that there is some change in the structure of the transition state, changes in its solvation upon introduction of the substituent. Naturally, in this case (with $E = \text{const}$) there was no reason to expect applicability of the Hammett equation to the reaction under study. It should be noted that

In the literature, although extremely rarely, there are studies of nucleophilic substitution reactions in which substituents affect the reaction rate specifically through a change in the entropy factor.

In the benzyl system such a phenomenon has been noted in several works (4–8); however, this fact has not yet been explained. For example, in Baker' s work (7) on the reaction of substituted benzyl halides with pyridine, the activation energy $E = 12.5$ kcal/mole does not change with the introduction of a substituent.

But the most striking fact is that the influence of substituents is completely analogous to that obtained in our case. Thus, para-substituents fall into the series

$$2,4\text{-}(NO_2)_2 \gg CH_3 > \text{tert.-}C_4H_9 > Hal \gtrless H > NO_2,$$

and the difference in the constants for the halides is negligible, while the change they produce in the constant of the unsubstituted compound is small. Introduction of one nitro group retards the reaction; however, the presence of two nitro groups in the 2,4-positions leads to instantaneous occurrence of the reaction.

Baker explains the result obtained by saying that the reaction rate is determined by two factors: rupture of the C–Br bond ("canionization," in the author' s terminology) and formation of the new C–N bond. The first factor predominates until strong orienting groups of the second kind (two nitro groups) are introduced. Within the framework of concepts of the mechanisms of nucleophilic substitution, it may be assumed that a transition occurs from the S_N2 mechanism to the S_N1 mechanism. The author did not verify this kinetically because of the instantaneous course of the reaction.

Fig. 2. Plot of the dependence $\lg K_2 = f\left(\frac{1}{T}\right)$ for $X = C_6H_4CH_2HgCl$ in dimethylformamide

Figure 1: Fig. 2. Plot of the dependence $\lg K_2 = f\left(\frac{1}{T}\right)$ for $X = C_6H_4CH_2HgCl$ in dimethylformamide

Fig. 2. Plot of the dependence $\lg K_2 = f\left(\frac{1}{T}\right)$ for $X = C_6H_4CH_2HgCl$ in dimethylformamide

An analogous phenomenon apparently occurs in the reaction of benzylmercuric chloride with iodine. Most likely, the mechanism of this reaction is not a "pure" S_E2, but lies in the intermediate region between the S_E2—S_E1 mechanisms. If, in the case of alkyl- and halogen-substituted benzylmercuric chlorides, the reaction mechanism is closer to S_E2, then introduction of a nitro group leads to rupture of the C–Hg bond becoming the dominant process, i.e., the mechanism approaches S_E1.

The influence of the methyl group from different positions of the benzene ring corresponds to its ability to donate electrons to the reaction center from these positions.

Introduction of halides in our case retards the process; moreover, from the meta position this effect is greater than from the para position, in accordance with the decrease in electron density at the reaction center caused by the substituents.

The study of the influence of substituents once again emphasizes the conventional nature of dividing mechanisms into the limiting cases S_N2 and S_N1 or S_E2 and S_E1.

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Note: Figure translations are in progress. See original paper for figures.